

Amines

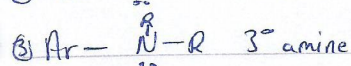
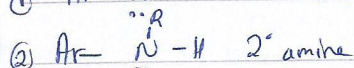
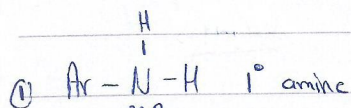
Aliphatic amines

$R-NH_2$ "alkylamine"

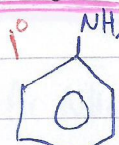
Aromatic amines

$ArNH_2$ "arylamine"

Aromatic Amines

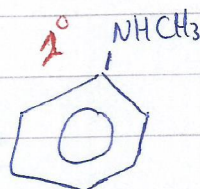


Nomenclature

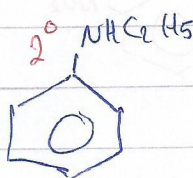


aniline

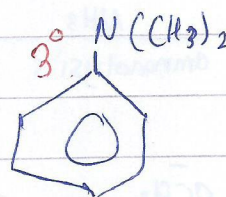
(benzene amine)



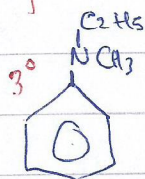
N-methylaniline



N-ethylaniline

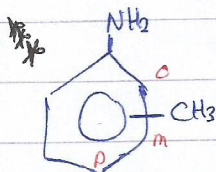


N,N-Dimethylaniline

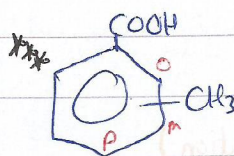


N-ethyl-N-methyl

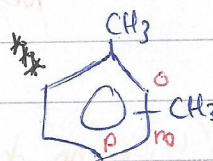
aniline



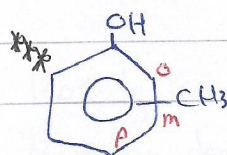
Toluidines



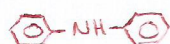
Toluic acid



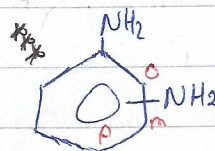
Xylenes



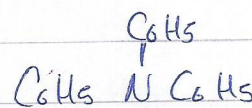
Cresols



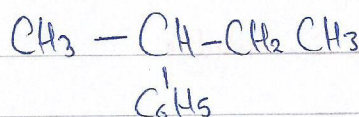
Diphenylamine



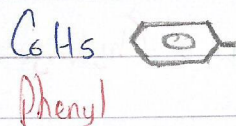
Phenylenediamines



Triphenylamine



2-phenylbutane



Phenyl



Phenylene

Synthesis of

1) By reduction of ArNO_2

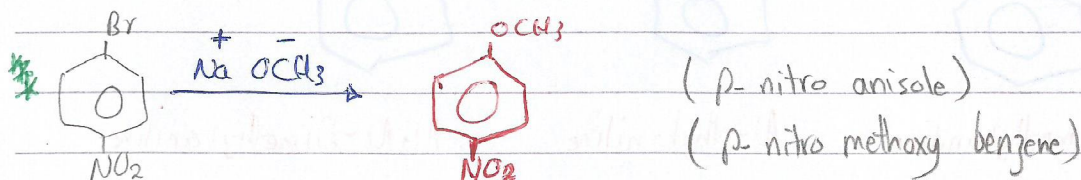
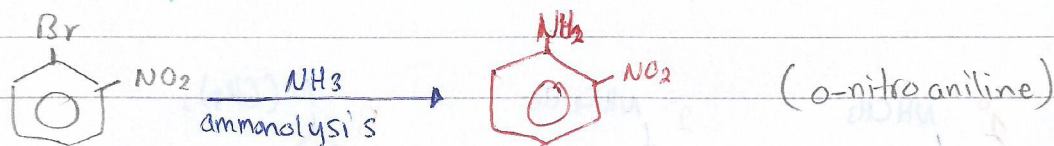
H_2/cat

H^+/M

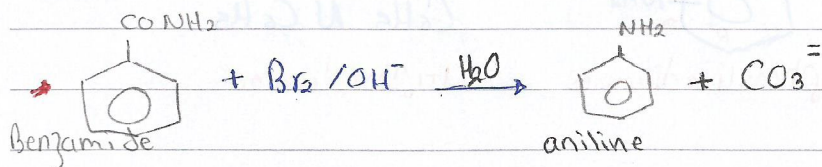
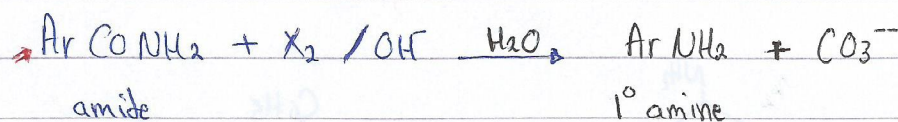
$\text{FeSO}_4/\text{OH}^-$

NH_4HS

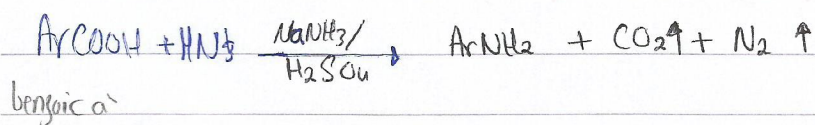
2) From by NH_3



3) From amides (Hofmann degradation)

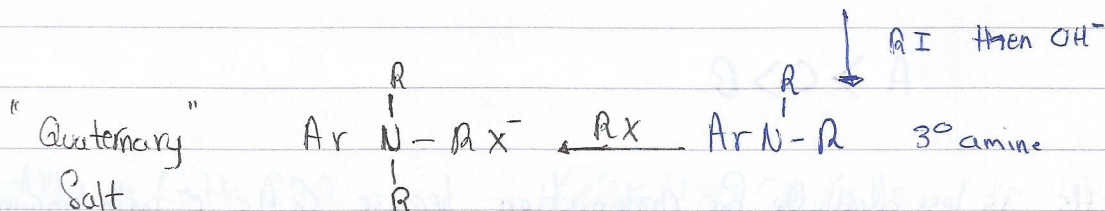
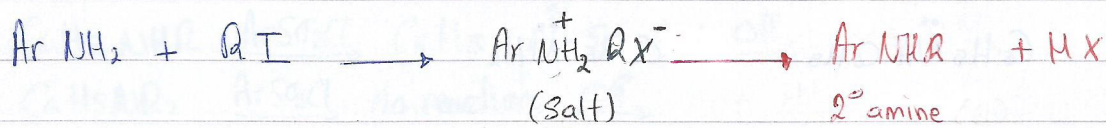


4) From ArCOOH by reaction with HN_3 (hydrazoic acid) weak α , unstable



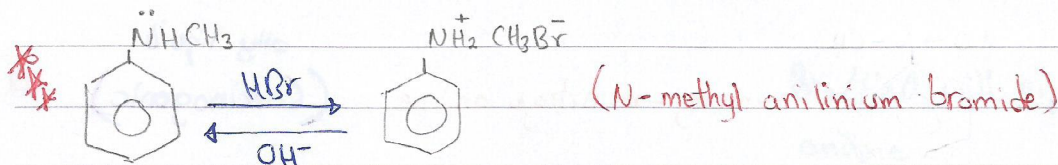
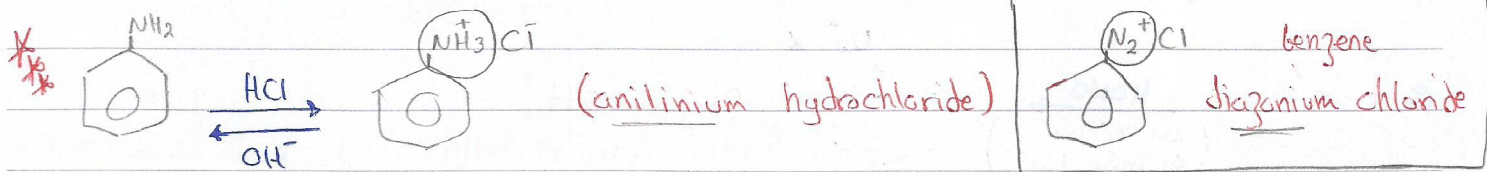
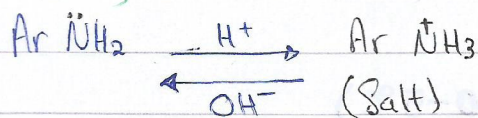
All the above ways are used to prepare 1° aromatic amines

5) For 2° and 3° amines by 1° amines alkylation of 1° amine



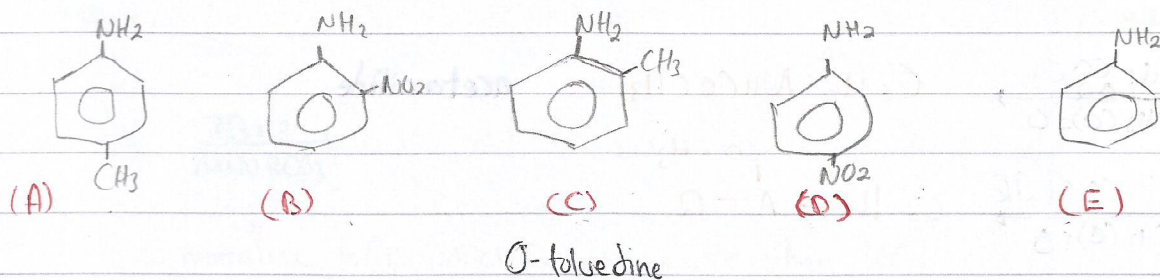
Reactions

1) Basicity



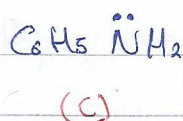
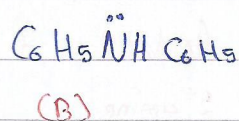
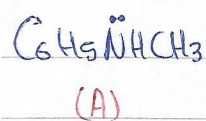
★ Basicity is increased by e⁻ donating gps and decreased by e⁻ withdrawing gps or e⁻
 ★ Maximum decrease by e⁻ withdrawing gps at ortho position } donating at o-position

~~✗~~ Arrange the following amines in a descending order according to basicity



A > E > C > D > B

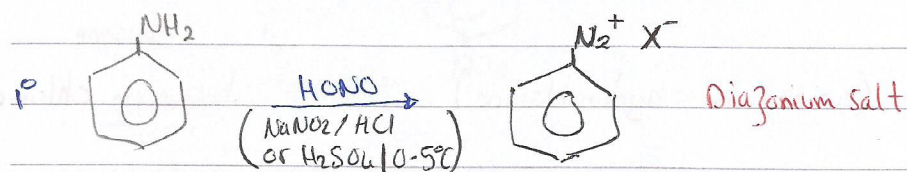
*** Arrange the following amine in a decreasing order according to basicity



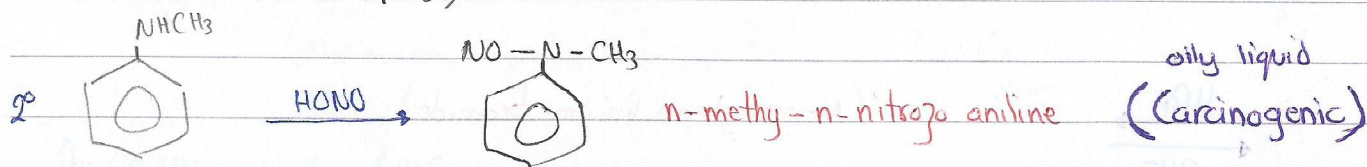
$\text{C}_6\text{H}_5\ddot{\text{N}}\text{H}\text{C}_6\text{H}_5$ is less available for protonation because C_6H_5 π withdrawing because it has resonance

2) Reaction with nitrous acid HNO_2 very unstable (Nitrosonation)

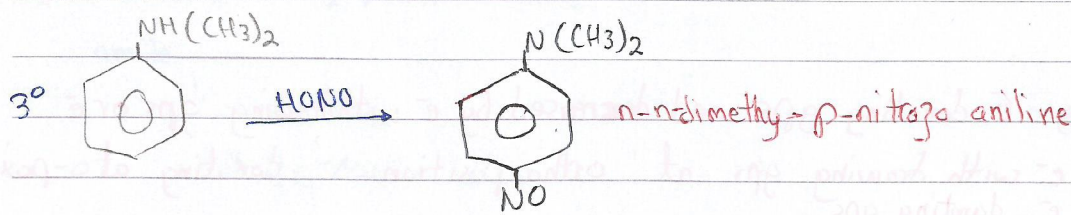
*** Nitrous acid prepared from $(\text{NaNO}_2/\text{HCl}$ or H_2SO_4 | $0-5^\circ\text{C}$)



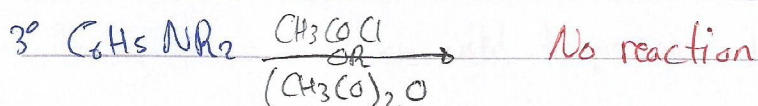
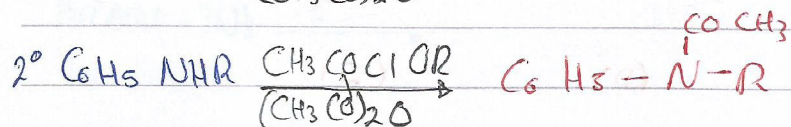
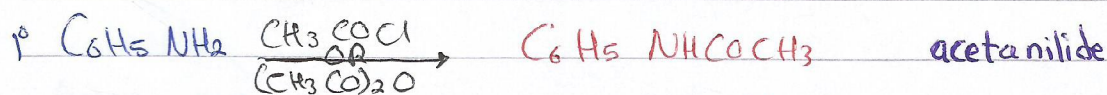
سائل غليظ



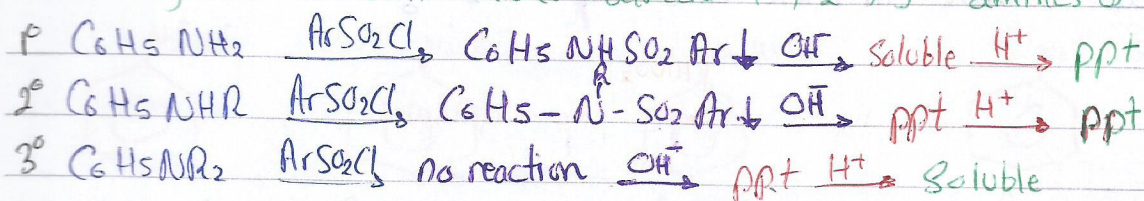
oily liquid (Carcinogenic)



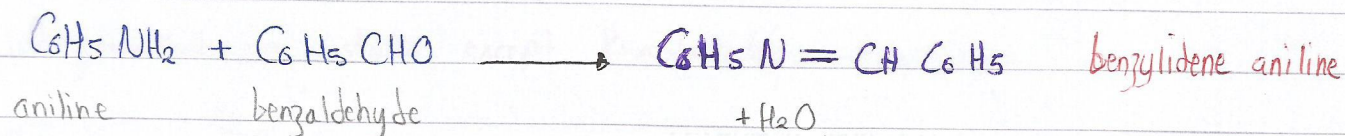
3) Acylation $\text{RCO}-$ acyl / $\text{CH}_3\text{CO}-$ acetyl



Hinsberg test to differentiate between 1°, 2°, 3° amines

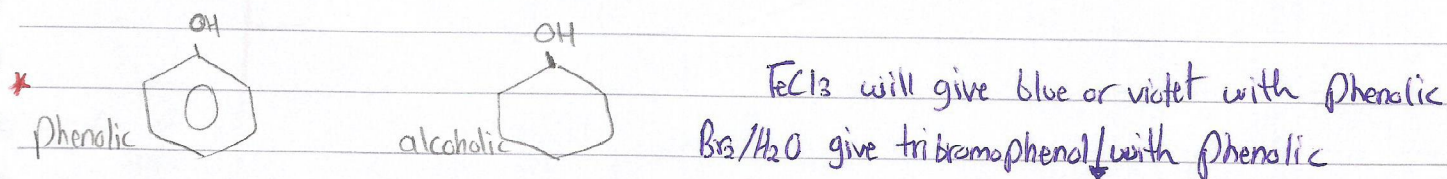
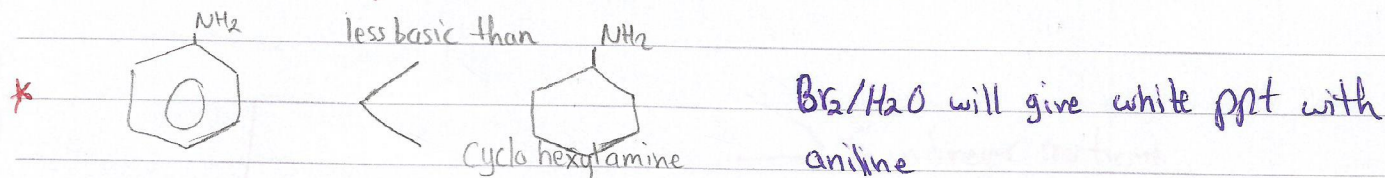


a) Formation of Schiff bases or anils for 1° amines



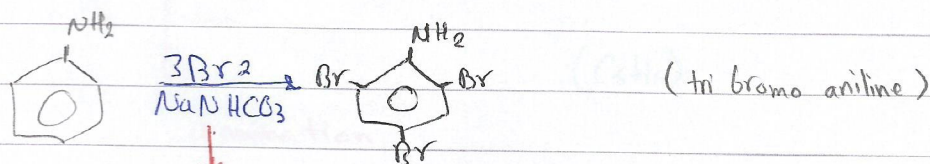
- C_6H_5- phenyl
- C_6H_4- phenylene, $\text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \rightarrow \text{p-phenyldiamine}$
- $\text{C}_6\text{H}_5\text{CH}_2-$ benzyl
- $\text{C}_6\text{H}_5\text{CH}=\text{C}$ benzylidene

* Protection of NH_2 by acetylation and Schiff base



* Strongly acidic reagents are unsuitable for substitution of aniline - Why?

Because acidic medium converts NH_2 to NH_3^+ which allows E^+ to attack m-position



to neutralize HBr which is more acidic than HCl

To prevent the

* How to differentiate between $ArNH_2$ and $ArNR_2$?

